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ICHTHYOL - ITS SOURCE AND PROPERTIES

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By O. C. Blade

ERRATA

The following corrections should be made in the above publication:

Page 3, line 11; reference (71) should be (71, p.3).
Page 6, table 1; footnote reference (78) should be (71).
Page 8, line 19; reference (71, p.35) should be (71, p.103).
Page 11, line 22; reference (123) should be (128).
Page 12, line 17; references (45,88) should be (44; 71, p.110).
Page 12, line 21; reference (162) should be (135).
Page 14, line 24; reference (96) was omitted.
Page 17, line 4 from bottom; reference (143) should be (117).
Page 23, reference (71); "p. 3" should be deleted.
References 18,28,29,34,65-69,73,118-123,137,142, in bibliography should show asterisks (*).

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UNITED STATES DEPARTMENT OF THE INTERIOR - BUREAU OF MINES

ICHTHYOL--ITS SOURCE AND PROPERTIES[1/]

By O. C. Blade[2/]

INTRODUCTION

The term "Ichthyol" is a name applied loosely to certain preparations used in pharmacy. These preparations do not occur as such in nature but are manufactured by various chemical processes. Ichthyol is the name trademarked for a product manufactured by the Ichthyol-Gesellschaft (Cordes, Hermanni & Co.) of Hamburg, Germany, and marketed in this country by Merck & Co., Inc., (5, 86, 87)[3/]. Although used in the literature rather loosely, the correctly applied word refers to the product obtained by sulphonating and then neutralizing with ammonia a distillate from the oil retorted from a certain high-sulphur bituminous shale found near the village of Seefeld in the Austrian Tyrol. Due to the fact that fossils of fish and marine animals occur in the limestone associated with the bituminous shale, these deposits have long been known as the "ichthyolite schists of Seefeld" (55). The Greek word "ichthys" for fish and the Latin word "oleum" for oil are the words from which the term is derived.

The crude, tarry shale oil, whose distillate is the raw material for the sulphonation process, has been referred to since the Middle Ages as "Dürsten" or "Tirschen" oil, and the term "ichthyol oil" has been used occasionally in the literature to designate the retorted crude oil (92, 93, 106, 117). The first application of the name "Ichthyol" to a particular product is credited to Schröter (35, 128). Various names for products manufactured by sulphonating bituminous distillates have been coined, and in some of these names the root from the word ichthys has been retained. Some of these names can be found in New and Nonofficial Remedies under the heading, Sulphoichthyolate Preparations and Substitutes (5).

The general term "Ichthammol" is used in the National Formulary of 1936 (7) to designate all preparations "obtained by the destructive distillation of certain bituminous schists, sulphonating the distillate, and neutralizing the product with ammonia." The same authority also defines as

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synonyms the terms "Bitumen sulphonatum, N.F.V.", and "Ammonium ichthosulphonate." These names refer only to the manufactured products in general as they are sold in commerce.

At times there has been a good deal of publicity concerning Ichthyol due to its rather unusual name and also because there was a shortage of the trade-marked material in this country during the World War. This publicity and the lack of reliable information about the product have given rise to the idea that a crude oil, tar, or shale that is peculiar in any way or contains an unusually large amount of sulphur must contain Ichthyol or similar products and therefore is very valuable. This idea is erroneous. To correct this misconception and to provide answers for the many inquiries that the Bureau of Mines receives on this subject, all the information readily available concerning Ichthyol has been collected and is presented here briefly. This report has been prepared and published by the Bureau of Mines in cooperation with the State of Oklahoma at the Petroleum Experiment Station at Bartlesville, Okla.

ACKNOWLEDGMENTS

The investigation was conducted under the general supervision of R. A. Cattell, chief engineer, Petroleum and Natural-Gas Division, Bureau of Mines, and N. A. C. Smith, supervising engineer, Petroleum Experiment Station, Bartlesville, Okla. The study was made under the direct supervision of Ludwig Schmidt, senior petroleum engineer, and H. M. Smith, petroleum chemist, Petroleum Experiment Station, Bartlesville, Okla.

The writer gratefully acknowledges the cooperation of Dr. Loyd Harris, of the Pharmacy School of the University of Oklahoma; J. L. Rader, principal librarian of the University of Oklahoma, and his staff of librarians in the Geology, Chemistry, Engineering, and Pharmacy Schools; Robert H. Dott, of the Oklahoma Geological Survey; Edward Bloesch, Tulsa, Okla.; Dr. R. U. Patterson, dean of the Oklahoma University School of Medicine and his library staff; and A. J. Kraemer, of the Bureau of Mines, in obtaining information and references concerning Ichthyol not available in the Petroleum Experiment Station library.

The letter dealing with the subject of Ichthyol is included with the kind permission of Dr. E. P. Schoch, of the Division of Industrial Chemistry of the University of Texas.

The paper was criticized and valuable suggestions were offered by Fred Dettelbach of Merck & Co. Inc., members of the personnel of the Division of Industrial Hygiene of the United States Public Health Service, Dr. C. J. Klemme of the School of Pharmacy, Purdue University, La Fayette, Ind., and by members of the Petroleum and Natural-Gas Division of the Bureau of Mines.

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HISTORY OF ICHTHYOL

Since ancient times, natural asphalts and tars have been used medicinally. Netolitsky (91) traces the present use of Ichthyol to the medicinal use of asphalt obtained from Egyptian mummies during the Middle Ages. In the mountainous region known as the Tyrol, in western Austria, crude tar from bituminous shale has been employed for centuries as a remedy for sores and wounds. Use of the crude material for healing purposes has been credited to Paracelsus (149). The natives of the region built primitive kilns for retorting the mineral, locally known as "Stinkstein", to obtain the tar, which had the legendary name of "Dürsten" oil or "Dürsten" blood.

The history of the shale industry of the Tyrol is very interesting. Hradil and Von Falser, in their book "Die Ölschiefer Tirols" (71), state that documentary evidence exists that the shale was processed in the neighborhood of Seefeld in 1350. The site of the earliest oil-shale industry, according to them, is in the Tyrol (71, Foreword). In that year, 1350, permission was granted by the court of Hartenburg at Telfs in Oberinntal to Berthold von Ebenhausen to produce the oil by distillation of the shale. In 1380 the privilege was awarded to Ulrich von Matsch. After 1600 distilling of the shale became more general. In 1839 a mine and works for the production of asphalt were established near Seefeld under the direction of Ferdinand Maximilian, Archduke of Austria. The project, known as the "Maximilianshütte", which absorbed a competitor, produced a good quality of asphalt that was widely used for years for paving, building, and plastering. In 1855 a refinery was erected in Scharnitz, a neighboring village of Seefeld, for the production of illuminating oil and naphtha. This industry gradually declined, as it could not compete with the lower-priced American petroleum products that became available soon after the drilling of the Drake well in 1859. The local peasants, however, continued to produce the tar for their own use as a household remedy.

Some time previous to 1882, Prof. Rudolph Schröter, a chemist of Hamburg, traveling in the region of Seefeld, became acquainted with the history and fame of the peculiar crude oil obtained from the Seefeld shale (35, 86, 87, 128). He succeeded in making a water-soluble product by sulphonating a portion of the distillate with concentrated sulphuric acid. The product was then neutralized with soda (later with ammonia) and the name Ichthyol applied. The product was given clinical tests by Dr. P. G. Unna, a dermatologist of Hamburg, and pronounced a valuable therapeutic for the treatment of skin diseases (141,142). In 1884 the Ichthyol Gesellschaft, Cordes, Hermanni & Co., of Hamburg, was organized, and the site of the Maximilianshütte and affiliated properties acquired (71, p.5). Patents on the sulphonation process were obtained by Schröter in 1885 (129, 130) and by Otto Helmers, chemist for the Ichthyol Gesellschaft, in 1892, 1894, and 1900 (58-60).

The production of substitutes came as a natural course, and other deposits in the Alpine area have been developed. Redfield (102) describes some of the development in Europe during and after the World War. In the

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United States the shortage of the genuine Ichthyol during that period spurred the production of substitutes. Materials prepared from some deposits of tarry sand or shale in Texas have been placed on the market at various times (5, 30, 36, 76, 112).

OCCURRENCE OF BITUMINOUS SHALES

In Europe, deposits of bituminous shale worked for medicinal purposes have been found scattered through virtually all sections of the Alps. The original area developed for the production of Ichthyol was the region in the Karwendel Mountains in the Tyrol, of which Innsbruck is the principal city and Seefeld, Reith, and Zirl are neighboring villages. Elsewhere in the Tyrol are found deposits, notably near Scharnitz, the Plansee and the Achensee (lakes), Munster, Kufstein, and Lienz (71, pp. 36-70). On the northern slope of the Karwendel Mountains in the Isar valley in Bavaria are numerous workings, and in the valley of the Loisach near Garmisch are outcrops that are being developed (107). In Switzerland in the Canton of Ticino, especially north of Meride on Lake Lugano, are deposits of "fish shales", which are exploited (54, 107). In certain areas of northern Italy bituminous shale deposits are mined, notably in the Trentino near Mollaro (17, 25, 26; 71, pp. 36-70) and on the south side of Lake Lugano in the provinces of Udine and Salerno (18, 84, 107). Some deposits of high-sulphur shale in France have been processed for pharmaceutical purposes, especially in the department of Ain (33, 34, 107).

Bituminous shales are the source of the oil from which Ichthyol is manufactured. These shales range in thickness from less than a foot to occasionally several yards, embedded in strata consisting of a mixture of marl, clay, and limestone (13). Hradil and Von Falser (71, p. 71) describe five types of bituminous strata of the Tyrol as listed by Sander (116):

Type 1. Seefeld. Finely divided strata of calcareous and sometimes sandy marl that contain less than 5 percent oil. Deposits of seams and lenses that contain 20 percent and more oil are interspersed throughout this marl. Large amounts of the poorer material are mined.

Type 2. Achensee. Strata somewhat similar to type 1. Due to the thin, lenslike character of the bitumen seams lying between layers of barren dolomite, the mines in these strata are few and relatively unimportant.

Type 3. Bächental. Thick seams of dark-brown marls with an oil content of 5 to 11 percent and containing more clay than the Seefeld type. These seams alternate with poor and barren marls. The mines of these strata are of noteworthy value.

Type 4. Haringer. A true bituminous marl (not bituminous shale) associated with coal seams. It is a compact, finely laminated marl of bright yellow to ocher color with a homogeneous distribution of bitumen. The oil content ranges from a trace to over 20 percent. These layers have been exploited in connection with the more recent mining of coal.

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Type 5. Mollaro. Continuous layers of dark-brown marl containing homogeneously distributed bitumen. It has been worked mostly in Southern Tyrol, now a part of Italy, where exploitation by mining is extensive.

The Seefeld shale, found in the upper Triassic formation, is the main source of material for Ichthyol. The veins usually are very steep and often folded. In the vicinity of Seefeld the deposits occur at altitudes of 3,000 to 6,000 feet.

Some of the bituminous marl obtained from this formation in the Seefeld mines is quite rich in oil of high sulphur content. It has been suggested by Hradil (67; 71, p. 35) that this material be named "Dirschenite." The term has been defined as the particular formation of bituminous marly shale obtained from the Triassic oil shales in the vicinity of Seefeld, from which an oil can be distilled that has a sulphur content of over 10 percent and consists of up to 50 percent thiophene compounds.

Hradil (67) and others (2, 3) state that bituminous shales of this type have been found nowhere else in the world. The geologic structures in which the bituminous shales occur in the Tyrol belong to the Mesozoic era. They are listed by Hradil (66) as the main dolomite of the upper Triassic formation, the Liassic series of the Jurassic, the upper Cenomanian series of the middle Cretaceous, and various strata in the Tertiary. If one consults the chart of Geologic Time and Formations (145), according to the nomenclature adopted by the International Geological Congress, the series in the Mesozoic era in Europe are seen to be quite different from those in North America. The highest part of the Triassic formation in Europe is the Rhaetic series and the next above is the Liassic series in the Jurassic formation. Neither of these series is listed in the respective formations in North America. Concerning the Rhaetic series and the limestone formations containing fossil impressions, Suess (133) states: "The Megalodus limestone and the Rhaetic series are not known outside the European area, except in the Himalaya and the outer chains of the Hindu Kush, in particular at Mount Sirban, near Abbotabad." Thus, although bituminous shales exist in other than the Rhaetic series, the indications are very strong that the "Ichthyolite" shales are peculiar to the region of the Alps.

Although the Rhaetic series is limited in area, deposits of material of that same period can be found in other localities. Suess (133, p. 269) states further: "Plant-bearing beds of Rhaetic age, on the other hand, are known in many places, e. g., Siberia, Turkestan, Tongking, Australia, in the Gondwana and Karoo series, in the Argentine Republic, and in the eastern part of the United States." The fact that some deposits might contain plant remains of Rhaetic age would not necessarily indicate that the shale is similar to that near Seefeld.

Although claims have been made that deposits from which Ichthyol may be manufactured occur in Russia (81, 85, 106), Poland (52), and the United States (36, 76, 93, 112), no definite proof has been published that such deposits contain material identical with that found in the Alpine area.

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In general, the shales of the Tyrol and of many other localities in the Alpine region occur in thin beds associated with marl and limestone. Their geologic formation places them as peculiar to the European area.

PHYSICAL AND CHEMICAL PROPERTIES OF BITUMINOUS SHALE IN THE TYROL

The oil shales of the Tyrol are described as rocks, generally dark-brown in appearance (66), having many layers ranging in color from light gray to yellow, brown, and black (13; 71, p. 71; 72). The wavy lines of folded layers in Seefeld shale are well-illustrated by photographs made by Hradil and Von Falser (71. pp. 29, 49, 50-51). The Seefeld deposits are described by Blumer (13) as gray to black bituminous shales in the Hauptdolomit (main dolomite) rich in fish impressions. Although the darker color usually indicates a richer shale, some exceptional types, such as Dirschenite, are yellowish-red and contain as much as 40 percent bitumen. The shales show a conchoidal fracture; the richer types have a fat, greasy luster, exude droplets of oil when lying in the sun, and have a characteristic odor variously described as aromatic, bituminous, "empyreumatic", and garliclike when rubbed, crushed, or heated (13; 71, pp. 71-72; 82). The shales burn in splinters with sooty flames and leave an ash that is white or yellow-brown to gray.

Shales from the various geologic and geographic locations in the Tyrol will show different analyses. Hradil and Von Falser (71, pp. 72-73) show that the specific gravity of the shale increases as the oil yield decreases. Of 48 samples tested, an oil yield of 50 percent was obtained when the specific gravity ranged from 1.3 to 1.4, while less than 1 percent of oil was obtained when the specific gravity was 2.8 and 2.9. Table 1 gives analyses of six samples of Seefeld shale by these authors:

TABLE 1. - Analyses of six samples of Seefeld shale[1/]

	Specific gravity	$CaCO_3+MgCO_3$ (HCl-soluble), percent	Clay (HCl-insoluble), percent	Oil yield, percent	Sulphur content of oil, percent
Black shale	2.115	67.3	10.5	10.6	9.49
Do.....	1.792	49.8	13.6	16.7	8.98
Dirschenite	1.451	34.2	11.3	37.7	13.45
Do.....	2.346	82.3	6.2	5.5	13.29
Do.....	2.257	77.1	4.5	9.3	13.95
Do.....	2.122	69.2	8.8	10.7	12.56

1/ Source: Hradil, G., and Von Falser, H., Die Ölschiefer Tirols: Leipzig, 1930, p. 35 (78).

Analyses of shale from the Tyrol and other localities in the region of the Alps have been published by various investigators (1, 12, 18, 34, 73, 78, 84, 92).

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In contrast with those of the marly shales of the Tyrol, the ashes of the shales of Scotland, Luxemburg, and Australia contain a high percentage of clay and a small amount of calcium and magnesium compounds (71, p. 75).

Summarizing, the shales of the Tyrol and similar shales in the Alps are characterized by thin, bituminous veins enveloped with layers of dolomite containing fossil impressions. The richer shales have a dark color and characteristic odor and burn readily. Analyses of the shales show that they vary widely in oil yield and that the inorganic material present has a high content of calcium and magnesium carbonates while the clay content is rather low. The sulphur content of the oil is relatively high.

PHYSICAL AND CHEMICAL PROPERTIES OF SHALE OIL OF THE TYROL

The oils obtained from shale of the Tyrol vary according to their source and with the method of retorting. The following description of properties is taken from the discussion by Hradil and Von Falser (71, pp. 96-108).

The crude oil is dark brown - nearly black - and in general appearance resembles tar. The odor is decidely empyreumatic (tarry), which is believed to be caused mainly by the high temperature of retorting. There also prevails a disagreeable, pungent odor reminding one of mercaptans and hydrogen sulphide. It is stated that the taste, which is described as sweetish and not unpleasant, was used by the peasants to determine quality and "genuineness." Specific gravity ranges from 0.89 to 0.98 for the average oils produced, although one sample of oil from "Dirschenite" had a specific gravity of 1.020.

The oil can be fractionated, provided special precautions are observed. Preliminary removal of the water usually is necessary, and the distillation must be carried out under reduced pressure to avoid excessive decomposition. The authors cited (71, pp. 101-102) made distillation analyses of a number of oils from different sources in the Tyrol using common distilling flasks. The results given for Seefeld oils are tabulated as follows:

TABLE 2. - Fractional distillation of Seefeld oil

Temperature	To 150°C.	150°-200°C.	200°-250°C	250°-300°C	Over 300°C.
Percent distilled.	4-11	10-27	14-21	22-45	-
Color	Water-white	Yellow-red	Yellow-red	Greenish	Brownish-green

No further figures were given, but the specific gravities were said to be in ascending order, and the first fractions were very fluid while the others became successively more viscous. All the fractions had a faint odor of hydrogen sulphide, but after this constituent was removed by treating, the odor became faintly aromatic. The heavier fractions were strongly fluorescent, and all the fractions darkened in a few hours on exposure to air and light. The distillation residue remaining was a black, almost solid, mass.

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During the distillation, a decomposition of sulphur compounds took place, with evolution of hydrogen sulphide and sulphur dioxide. There was also a precipitation of elementary sulphur, which gave a milky appearance to the trace of water set free.

According to Baumann and Schotten (9), the oil fraction used by Schröter to prepare his original Ichthyol was clear and brownish-yellow, had a specific gravity of 0.865, and boiled between 100° and 255°C., as follows: 100°-120°C., 6 percent; 120°-160°C., 53 percent; 160°-225°C., 33 percent; 225°-255°C., 6 percent. The fractions possessed a characteristic odor suggesting mercaptans and petroleum hydrocarbons.

Chemically, shale oil from the Tyrol consists principally of carbon, hydrogen, sulphur, and small amounts of nitrogen and oxygen. Baumann and Schotten (9) published the first elementary analysis of Seefeld shale oil in 1883. The fraction boiling between 100° and 255°C. with a specific gravity of 0.865, had the following values: Carbon, 77.25 percent; hydrogen 10.52 percent; sulphur, 10.72 percent; nitrogen, 1.10 percent. The sulphur content of oils from various sources might range between 1 and 12 percent, which is reflected by corresponding changes in carbon and hydrogen content (71, p.103). Hradil and Von Falser (71, p.35) compare the above analysis with Engler's elementary analysis of petroleum and Köhler's analysis of asphalt. The values are given in the following table.

TABLE 3. - Elementary analyses of petroleum, asphalt, and Seefeld shale oil, percent 1/

	Carbon	Hydrogen	Oxygen	Sulphur	Nitrogen
Petroleum (Engler)	83-86	11-13	0-3	Traces to 3	Traces to 2
Asphalt (Köhler)	78.80-89.28	8.66-13.20	0.40-0.66	1.13-10.00	0.09-1.58
Seefeld shale oil (Baumann-Schotten).....	77.25-77.94	10.5	-	10.72	1.1

1/ Source: Hradil, G., and Von Falser, H., Die Ölschiefer Tirols: Leipzig, 1930, p. 103.

The extremely unsaturated nature of shale oils from the Tyrol is shown by their reactions toward various reagents (71, pp. 105-108). Most of the crude oils and their distillates react with concentrated sulphuric acid with the liberation of heat and evolution of sulphur dioxide to form dark resinous masses, with the exception of the oil from the Häringer strata, which reacts less readily. This latter oil is supposed to contain a larger proportion of hydrocarbons of the paraffin series and is therefore less reactive.

Concentrated nitric acid reacts with the shale oils of the Tyrol with extreme violence. Scheibler (117) states that he was unable to determine sulphur content by the Carius method because the material burst into flames, with consequent damage to the tubes. With less acid and with chilling, reaction with nitric acid takes place to form a reddish-yellow viscous mass.

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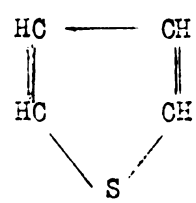
Concentrated hydrochloric acid, on the other hand, reacts only with the basic material present. Its action is very mild, and the acid becomes dark brownish-red.

Potassium permanganate solution is strongly reduced, and both iodine and bromine are easily taken up. The iodine numbers of six Seefeld oils, as determined by Helmers, ranged from 87.1 to 112.7 (71, p. 107). The crude oils and their distillates are easily oxidized by exposure to air and the odor becomes more mild (71, p.107).

A high sulphur content is characteristic of shale oils of the Tyrol. According to Hradil and Von Falser (71, pp.99-100, 104), the heavier oils have a higher percentage of sulphur and oils with a specific gravity near 1 contain 6 to 7 percent of sulphur. The Seefeld oil is said to be exceptionally rich in sulphur. Its average specific gravity is 0.944 to 0.965 and its sulphur content amounts to 7 to 10 percent. The highest sulphur content noted was 16.36 percent in a Seefeld shale oil of specific gravity 1.020 obtained from Dirschenite (71, p.99).

The sulphur is believed to be present in the oil in three forms - as hydrogen sulphide, formed during retorting; as free sulphur; and as organically combined sulphur in the sulphidic, unoxidized form (71, p.104). It is the latter type that is believed to be responsible for the therapeutic value of both the crude oil and the manufactured Ichthyol (44; 71, p.110). Judging from the high content of this organically combined sulphur in the oil and its distillates, the sulphur compounds must constitute a considerable portion of the oil. Fränkel (44) believed that these compounds, in addition to being unoxidized, were unsaturated and of a cyclic nature. He even offered the suggestion that they might be thiophenes.

Thiophene is an unsaturated ring compound with the formula,



Numerous derivatives, in which the hydrogen atoms are replaced by groups of carbon and hydrogen atoms, are known. The presence of thiophene derivatives in shale oils of the Tyrol was definitely established by Scheibler. In a series of papers (117-125) he has described his method of purification and isolation of definite derivatives of thiophene. Briefly, the crude oil was first treated with dilute sulphuric acid, heated with sodium, and then treated with Grignard reagent and sodium. The oil thus treated was light-yellow and of pleasant odor and contained only carbon, hydrogen, and sulphur. Tests of this oil with phenanthrene-quinone and sulphuric acid gave a violet-red color, an indication of thiophene derivatives. The same test with thiophene itself produces a green color and is known as the Laubenheimer reaction (71, p.104; 117).

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The treated oil was distilled under reduced pressure without decomposition. Close fractionation and tests on the largest fractions with aluminum chloride and acetyl chloride established the presence of several derivatives of thiophene that were found to be isomers of propyl- and butylthiophene. Confirmatory tests with semicarbazone were made to find the crystalline compounds of definite melting point. Tests with mercuric chloride also produced precipitates characteristic of thiophene compounds.

Scheibler estimated that the crude oils he tested contained as much as 50 percent of thiophene compounds. The balance he considered to be chiefly aromatic hydrocarbons, with smaller amounts of indenelike hydrocarbons, phenols, organic acids, and mercaptans. Concerning the thiophene derivatives, Hradil and Von Falser (71, p.105) emphasize that this type of sulphur compound is found only rarely in petroleum, and then in very small amounts (a few tenths of 1 percent), and in coal tars only to about 0.5 percent.

Summarizing, the shale oils of the Tyrol are dark, heavy tars with a specific gravity close to 1 and a decidedly tarry and somewhat unpleasant odor. The oils cannot be distilled without excessive decomposition unless they are given special treatment beforehand and reduced pressure is used. The fractions are fluorescent and, like the crude oil, oxidize easily on exposure to air. Analysis of the shale oil shows its main constituents to be carbon, hydrogen, sulphur, and small amounts of nitrogen and oxygen. The oil is extremely unsaturated and has a high content of sulphur, which may be partly explained by the large proportion of thiophene compounds. Other compounds believed to be present are aromatic hydrocarbons, phenols, organic acid and mercaptans.

PRODUCTION AND REFINING OF SHALE OIL OF THE TYROL

The deposits of the Tyrol, steeply inclined and very often folded, are exploited by modern mining methods. Formerly, the outcroppings of the veins were worked almost entirely by open pits, and, due to climatic conditions at the high altitude of the mines, material was obtained only during the summer months (13). Tunnels are now driven into the mountainside, and the strata at a given level are followed as far as practicable. The diagrams of Hradil and Von Falser (71, pp.41-42, 45-48) give a good description of the workings in the region of Seefeld. After removal from the strata, the less valuable portions of the shale are eliminated by a system of grading, and the stone is broken to pieces about the size of the palm of the hand (35, 86, 87). For the manufacture of Ichthyol,[4] shales containing different percentages of sulphur are chosen to produce an oil of 13 percent sulphur, so that the finished product itself will be uniform in sulphur content (146, 147).

Actual data on the retorting of Tyrol shale have not been obtained. The details of the processes are supposed to be trade secrets suited to the type of shale retorted and products to be obtained. The very early methods consisted of heating the shale in primitive kilns, while later, in the 1850's, processes were used similar to that for obtaining tars from oil shales and lignites for the production of illuminants and paraffin (24, 98, 136).

4/ Private communication.

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For many years the peasants of the Tyrol have retorted shale by a method of downward distillation (71, pp.82-83; 82). The container, which is a cast-iron pot shaped very much like a crucible, is filled with shale and inverted over a perforated base connected to pipes leading downward and out (71, pp.84-86; 82). A number of these crucibles are contained in a single furnace heated by the combustion of a convenient fuel, very often wood. Burning takes place from the top down, and the oil, which is set free as tar and vapors, passes downward and collects in a cooled vessel.

No information is available concerning the methods of fractionation used. In view of the difficulty Scheibler experienced when first he attempted to distill the crude oil, it is certain that preliminary treatment or extra precautions must be taken with an oil that contains water and is so easily decomposed by heat (71, p.105; 117). Scheibler's experiments would indicate that the fraction richest in thiophene homologues corresponds to that which he obtained from the purified oil boiling at 160°-190°C. at an absolute pressure of 360 mm.

The process of sulphonation consists generally of treating the oil with an excess of concentrated or even fuming sulphuric acid. The reaction, as would be expected, is very vigorous. Evolution of sulphur dioxide takes place with a rise in temperature, which must not be too high or the final product will be inferior in therapeutic value (113).

In his original method, Schröter (123) treated the oil with an excess of concentrated sulphuric acid. The temperature rose to 100°C. and there was copious evolution of sulphur dioxide fumes. Neutralizing was done with soda and was followed by washing to remove the impurities (9). Three well-defined liquid layers were formed, of which the top was the unsulphonated oil, the middle a viscous, dark, ropy precipitate, and the bottom a reddish water solution. The top and bottom layers were removed, and more water was added to the remaining material until it was completely dissolved. The neutralized "Ichthyol sulphonic acid" was then precipitated again by the addition of sodium chloride ("salted out") (131).

Summarizing, the production and refining of shale oil of the Tyrol consist, briefly, of retorting in special equipment the shale obtained by tunnel mining methods. A primitive form of downward distillation has been employed by the natives for many years. Preliminary treatment of the resulting tarry oil and fractionation under carefully controlled conditions is necessary because of its unstable composition. Fractions are treated with an excess of sulphuric acid, then neutralized, washed, and further purified to make water-soluble products of therapeutic value.

DESCRIPTION AND COMPOSITION OF ICHTHYOL

Ichthyol is a soft, semisolid, dark-brown or black material with a characteristic bituminous odor and a burning taste. Its specific gravity is approximately 1, and in consistency Ichthyol is about like molasses. The organic substance is soluble in water and partly so in alcohol or ether alone, but completely soluble in a mixture of equal volumes of ether and alcohol.

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Residue obtained by evaporation at 100°C. is about 53 percent by weight. When the material is strongly heated, ammonia is driven off and there is considerable carbonizing. Incineration leaves no ash. The water solution of Ichthyol is faintly acid and reacts with many inorganic salts and mineral acids to produce a precipitate of resinous appearance.

Numerous analyses of Ichthyol have shown it to contain approximately 3 percent total ammonia, of which about 1.6 percent is in the form of ammonium sulphate and 1.4 percent is combined with the complex ichtho-sulphonic acids and approximately 10 to 11 percent total sulphur, of which about 4 to 4.5 percent represents "oxidized" or introduced sulphur and the remainder, 5.5 to 7 percent, is "organic" or "sulphidic" sulphur.

It has been stated that a preparation such as Ichthyol contains sulphur in three forms: 1, combined sulphur naturally occurring in the distillate ("organic" or "sulphidic" sulphur), which is believed to be the therapeutically active constituent; 2, sulphur introduced by sulphonating the distillate, which provides the sulphonic acid radical, making the product water soluble (45, 88); and 3, sulphur, chiefly in the form of ammonium sulphate, resulting from neutralization with ammonia and incompletely removed by the purification process.

Based essentially on methods developed by Von Hayek (56) and by Thal (162), standard methods of analysis of preparations such as Ichthyol were developed in cooperation with the manufacturers by chemists of the American Medical Association. The following descriptions of the analytical methods adopted are taken from the report by Puckner (105) published in 1912:

> Total ammonia. - If 25 cc of potassium hydroxide test solution and 100 cc of water be added to from 5 gm to 6 gm of Ichthyol previously weighed into a distilling flask, the mixture distilled until no more ammonia passes over, the distillate collected in 15 cc of normal sulphuric acid to which 1 drop of methyl orange test solution has been added, and the excess of acid then titrated with tenth-normal potassium hydroxide, the amount of normal sulphuric acid consumed should correspond to from 2.75 percent to 3.75 percent of total ammonia (NH_3).
>
> Ammonium sulphate. - If from 5 gm to 6 gm of Ichthyol be weighed into a graduated flask of 500 cc-capacity, diluted with 50 cc of water, 10 cc of a 10-percent solution of albumin added, followed by 5 portions of 5 cc each of diluted hydrochloric acid, shaking after each addition, the mixture made up to a volume of 500 cc and filtered through a dry filter; and if 200 cc of the filtrate be heated to boiling, 10 cc of barium chloride solution added, the mixture allowed to stand for 24 hours, the precipitate of barium sulphate collected, heated, and weighed in the usual way; the weight of barium sulphate obtained should correspond to from 5.7 percent to 6.2 percent of ammonium sulphate.

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Total sulphur. - If from 0.5 gm to 1 gm of Ichthyol be weighed into a Kjeldahl flask diluted with 30 cc of water, 5 gm of potassium chlorate added, followed by 30 cc of nitric acid, the mixture evaporated to about 5 cc, 25 cc of hydrochloric acid added, this solution evaporated to about 5 cc, 25 cc of hydrochloric acid again added, this solution evaporated to about 5 cc, 100 cc of water added, the solution heated to boiling, 10 cc of barium chlorid solution added, the mixture allowed to stand for 24 hours, the precipitate of barium sulphate collected, heated, and weighed in the usual way, the weight of barium sulphate should correspond to at least 10 percent of total sulphur.

"Ichthosulphonic" sulphur. - If the sulphur contained in the ammonium sulphate, as previously determined, in Ichthyol be calculated and the result subtracted from the "total sulphur", as previously determined, the remainder should represent the sulphur present in the compound both in the organically combined state and in the "sulphonic" form.

"Sulphonic" sulphur. - If the ammonia contained in the ammonium sulphate, as previously determined, in Ichthyol be calculated and the result subtracted from the "total ammonia", the remainder should represent the ammonia combined with the ichthosulphonic acids in the substance. If this value be multiplied by 1.88, the result should represent the sulphur present in the sulphonic acids in an oxidized state, i.e., the "sulphonic sulphur."

"Organic" ("sulphidic") sulphur. - If the "sulphonic" sulphur in Ichthyol, as previously calculated, be subtracted from the "ichthosulphonic" sulphur, as previously calculated, the remainder should correspond to at least 5.5 percent of "organic" ("sulphidic") sulphur.

Although various methods have been developed for the determinations of ammonium sulphate and total sulphur content (4, 63, 97, 135), the several forms in which the ammonia and sulphur are present are calculated from three determinations - total ammonia, ammonium sulphate, and total sulphur - as described in the procedures quoted. An example, with symbols, is here shown to illustrate the methods of calculation, using the results of an analysis given by Puckner (105):

	Percent
A = total ammonia	3.01
B = ammonium sulphate	6.39
C = total sulphur	10.27
B x 0.258 = D, ammonia in ammonium sulphate.....	1.65
A - D = E, ammonia in ichthosulphonic acids	1.36
E x 1.88 = F, "sulphonic" sulphur	2.56
B x 0.242 = G, sulphur in ammonium sulphate	1.55
C - G = H, ichthosulphonic sulphur	8.72
H - F = I, "organic" or "sulphidic" sulphur	6.16

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The final result of the calculations, represented by the symbol I, the determined values, A, B, and C, and the physical and chemical properties first noted are the basis for standards of composition of Ichthyol and substitutes.

Based on the dehydrated residue, the total sulphur content of Ichthyol amounts to around 19 percent, of which the sulphonic sulphur is approximately 5.5 percent and the "organic" or "sulphidic" sulphur is around 13.5 percent (15, 53, 96, 135). Baumann and Schotten (9) in 1883 gave the following elementary analysis of the dry soda neutralized material; carbon, 55.05 percent; hydrogen, 6.06 percent; sulphur, 15.27 percent; sodium, 7.78 percent; and oxygen, 15.83 percent. On this basis, a formula was tentatively assigned to Ichthyol, but it has since been proved that Ichthyol is a complex mixture and not a definite chemical compound (61, 96, 105).

Originally, the term Ichthyol referred most generally to the sodium product; it is now the trademarked name for the ammonium-neutralized material (9, 88, 128). The sodium and other modifications are known by such names as Ichthosodium, Ichthocalcium, and Sulpho-Ichthyolate (sodium), (calcium), etc. (87).

Although there are slight variations in the analyses of Ichthyol, there are marked differences between it and its substitutes. Thus, the total sulphur content, the relative amounts of several forms of sulphur, and the values of other properties vary considerably, depending principally on the source of the raw material. Numerous comparisons of Ichthyol with various substitutes have been published (8; 11; 14; 56; 71, p.112; 105; 115; 135; 139).

USES OF ICHTHYOL

From its very introduction, Ichthyol has been used largely as an external application for skin diseases and inflammations. It is incorporated with other materials as a constituent of ointments and salves or diluted with water if used alone. It is mildly antiseptic and is claimed to be soothing to inflamed tissue (88).

Numerous modifications of Ichthyol have been developed for specific purposes. Three of the more common types are described briefly. Ichthargan or Ichthyol-silver is obtained by treating the sulphonated product with silver oxide. The finished product is a brown powder soluble in water, glycerine, and dilute alcohol and contains 30 percent silver and 15 percent organic sulphur (75, 88). Ichthalbin or Ichthyol-albumen is the product of the sulphonated material and albumen. It is described as a fine grayish-white powder, odorless, tasteless, and insoluble in water (60, 88, 131). Ichthoform or Ichthyol-formaldehyde is the formaldehyde reaction product of the acidified oil. It is a blackish-brown, odorless powder insoluble in water or alcohol (88, 131). A list of the modifications of Ichthyol can be found in the National Dispensatory and other sources (53, 88).

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ECONOMIC CONSIDERATIONS

The market value of Ichthyol is determined by such economic factors as supply and demand and the cost of production. The present (1938) wholesale price of Ichthyol as quoted in the Oil, Paint, and Drug Reporter is $4 to $4.25 per pound (94). Most of the substitutes are priced somewhat lower.

If the supply of crude material alone governed the price of the finished product, it would not require a great amount of domestic production to reduce the average price considerably. Zublin (149) points out that if components for the manufacture of a material identical with Ichthyol could be obtained easily from petroleum, the production from one small well would be sufficient to flood the market. The expense of processing must be considered in arriving at manufacturing costs of this type of material. Besides the production, fractionation, and purification that is required, the oil must be treated with greater than its own volume of pure sulphuric acid in concentrated form followed later with a neutralizing agent.

Only a small volume of sulphonated bituminous materials, such as Ichthyol and various substitutes, which are prepared for medicinal purposes, is imported into this country. By Acts of Congress in 1897; 1909, and 1913 this type of material, but not the modifications, was held exempt from duty (144). In the following table are listed the imports from 1909. It must be borne in mind that imports not only of the trade-marked Ichthyol but also of competitive products are contained in the table under the general term "sulphonated bitumen."

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TABLE 4. - Imports of sulphonated bitumen (Ichthyol and substitutes) into the United States, 1909-1937[1]

Fiscal year	Quantity, pounds	Value	
		Total	Per pound
1909	74,217	$ 113,494	$ 1.53
1910	14,379	21,485	1.49
1911	39,745	59,504	1.50
1912	49,872	72,184	1.45
1913	44,347	61,796	1.39
1914	66,957	92,485	1.38
1915	51,847	70,664	1.36
1916	69,227	59,470	.86
1917	91,884	60,757	.66
1918	65,982	43,541	.66
1919	19,623	9,830	.50
1920	98,135	79,133	.81
1921	76,135	107,752	1.42
1922	74,330	89,150	1.20
1923	20	15	.75
1924	9,300	17,058	1.83
1925	12,430	12,941	1.04
1926	25,396	34,385	1.35
1927	48,199	58,821	1.22
1928	42,610	60,321	1.42
1929	32,529	42,066	1.29
1930	20,980	29,272	1.40
1931	10,462	15,607	1.49
1932	3,082	4,615	1.50
1933	3,380	4,740	1.40
1934	13,285	18,842	1.42
1935	-	-	-
1936	5,948	1,397	0.23
1937[2]	1,390	536	0.39

1/ Sources: U. S. Tariff Commission, Tariff Information Surveys: Washington, 1921, p. 94.
Foreign Commerce and Navigation, U. S. Department of Commerce, Washington, D. C.

2/ Preliminary, subject to revision.

No statistics are available concerning the domestic production of sulphonated oils and bitumens for medicinal purposes.

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DISCUSSION

It is important to keep in mind that ichthyol and related products are manufactured substances. In other words, ichthyol does not occur, it is made. While the source of the original material is a peculiar shale in the Austrian Tyrol, other deposits have been developed. In this country, products for medicinal use prepared from tarry sands and refinery acid sludges have been put on the market under various trade names (5; 36; 95, p.628) Experiments were conducted by Baxter and Dumont on sulphonating oil from Colorado shale, but their results were inconclusive (10). Data from other sources concerning sulphonation of fractions from high-sulphur crude oil indicated that products having a sulphur content comparable with Ichthyol were possible. In both of these instances, no attempt was made to determine the therapeutic value.

The Division of Industrial Chemistry at the University of Texas has investigated the question of obtaining ichthyol substitute from crude oil. The following statement is their form reply to inquiries on this subject:

> We have received a letter from you in reference to Ichthyol. We doubt sincerely that there is any Ichthyol in your sample. Ichthyol is not found as such in the ground: it is a material made from a special kind of distillate obtained in Europe from a bituminous shale containing animal remains. The main point about Ichthyol is the manufacture, and since it is not a substance of uniform composition, it is undoubtedly manufactured in various different ways. Not only does it differ in its manner of manufacture, but it is likely, also, that different kinds of crude-oil distillates may be used for this purpose. The mere fact that a crude petroleum has an odor similar to Ichthyol and is similar to it in appearance, is absolutely no indication that it contains the raw material necessary for the manufacture of Ichthyol. The raw oil used for the manufacture of Ichthyol has a totally different appearance; it has more nearly the properties of kerosene than anything else that we are ordinarily familiar with. There is nothing definitely known about the kind of crude material that is best to be used for the manufacture of Ichthyol, and the manufactured article now found in the market is probably produced by various different methods. We believe the whole search after Ichthyol to be as useless as the search after some of these buried treasures with which every community is familiar.
>
> A thorough examination to decide whether or not your material could be used to make Ichthyol would cost from $250 upward. All lesser attempts are worthless.

The work of Scheibler (143), the suggestion of Fränkel (19, p.129; 44), and the discussions by Hradil and Von Falser (71, pp.96, 103-106, 110-111) present the idea that the high percentage of thiophene compounds in Seefeld shale oils is largely responsible for their therapeutic value. However, it

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is not within the scope of this paper to pass on the possible connections between the chemical constitution of the shale oils of the Tyrol and their reputed therapeutic value. Considerable research on the constitution of the peculiar shale and the retorted oil from which Ichthyol is obtained is necessary to determine further the compounds present and their therapeutic significance.

Clinical examination, as well as evaluation of chemical properties, is essential for determining the medicinal value of such a complex preparation as Ichthyol. Doctor Unna (141, 142), as stated previously, made tests to determine the therapeutic value of Ichthyol. Clinical tests on new preparations are very often tedious, but no claims for medicinal value should be made until they have been conducted with favorable results.

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